# REDOX REACTION

**Introduction :**

Redox reactions shows vital role in non renewable energy sources. In cell reactions where oxidation and reduction both occurs simultaneously will have redox reaction for interconversion of energy.

**Redox Reaction (Oxidation-Reduction) :**

Many chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed as **oxidation-reduction** or **redox reactions.**

Or

Those reactions which involve oxidation and reduction both simultaneously are known as oxidation reduction or redox reactions.

Or

Those reactions in which increase and decrease in oxidation number of same or different atoms occurs are known as redox reactions.

**Oxidation State :**

Oxidation state of an atom in a molecule or ion is the hypothetical or real charge present on an atom due to electronegativity difference.

Or

Oxidation state of an element in a compound represents the number of electrons lost or gained during its change from free state into that compound.

**Some important points concerning oxidation number :**

**(1)** Electronegativity values of no two elements are same –

$P > H \quad C > H \quad S > C \quad Cl > N$

**(2)** Oxidation number of an element may be positive or negative.

**(3)** Oxidation number can be zero, whole number or a fractional value.

Ex. $Ni(CO)_4 \Rightarrow$ O.S of Ni = 0

$N_3H \Rightarrow$ O.S of N = −1/3

$HCl \Rightarrow$ O.S of Cl = −1

**(4)** Oxidation state of same element can be different in same or different compounds.

Ex. $H_2S \Rightarrow$ O.S of S = −2

$H_2SO_3 \Rightarrow$ O.S of S = +4

$H_2SO_4 \Rightarrow$ O.S of S = +6

**Some helping rules for calculating oxidation number :**

**(A) In case of covalent bond :**

**(i)** For homoatomic molecule

$$\begin{array}{lcccccc} & A & - A & A & = A & A & \equiv A \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{O.N. :} & 0 & 0 & 0 & 0 & 0 & 0 \end{array}$$

**(ii)** For heteroatomic molecule (EN of B > A)

$$\begin{array}{lcccccc} & A & - B & A & = B & A & \equiv B \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{O.N. :} & +1 & -1 & +2 & -2 & +3 & -3 \end{array}$$

**(iii)** The oxidation state of an element in its free state is zero. Example- Oxidation state of Na, Cu, I, Cl, O etc. are zero.

**(iv)** Oxidation state of atoms present in homoatomic molecules is zero.

Ex. $H_2$ , $O_2$ , $N_2$ , $P_4$ , $S_8$ = zero

**(v)** Oxidation state of an element in any of its allotropic form is zero.

Ex. $C_{Diamond}$ , $C_{Graphite}$ , $S_{Monoclinic}$ , $S_{Rhombic}$ = 0

**(vi)** Oxidation state of all the components of an alloy are 0.

Ex. $\underset{0}{\overset{(Na}{\downarrow}} - \underset{0}{\overset{Hg)}{\downarrow}}$

**(vii)** In complex compounds, oxidation state of some neutral molecules (ligands) is zero.

Ex. CO, NO, $NH_3$, $H_2O$.

**(viii)** Oxidation state of fluorine in all its compounds is –1.

**(ix)** Oxidation state of IA & II A group elements are +1 and +2 respectively.

**(x)** Oxidation state of hydrogen in most of its compounds is +1 except in metal hydrides (-1)

| | | | | |
|---|---|---|---|---|
| Ex. | NaH | LiH | $CaH_2$ | $MgH_2$ |
| | ↓ ↓ | ↓ ↓ | ↓ ↓ | ↓ ↓ |
| O.S. : | +1 –1 | +1 –1 | +2 –1 | +2 –1 |

**(xi)** Oxidation state of oxygen in most of its compounds is -2 except in -

(a) Peroxides $(O_2^{-2}) \rightarrow$ Oxidation state (O) = -1

Ex. $H_2O_2$ , $BaO_2$

(b) Super Oxides $(O_2^{-1}) \rightarrow$ Oxidation state (O) = -1/2

Ex. $KO_2$

↓

-1/2

(c) Ozonide $(O_3^{-1}) \rightarrow$ Oxidation state (O) = -1/3

Ex. $KO_3$

↓

-1/3

(d) $OF_2$ (Oxygen difluoride)

F – O – F

↓

Oxidation state (O) = + 2

(e) $O_2F_2$ (dioxygen difluoride)

↓

Oxidation state (O) = + 1

**(xii)** Oxidation state of monoatomic ions is equal to the charge present on the ion.

Ex. $Mg^{+2} \rightarrow$ Oxidation state = +2

**(xiii)** The algebric sum of oxidation state of all the atoms present in a polyatomic neutral molecule is 0.

Ex. $H_2\underline{S}O_4$

If O.S of S is x then

2 (+1) + x + 4 (-2) = 0

x - 6 = 0

x = +6

Ex. $H_2SO_3$

If O.S of S is x then

$2(+1) + x + 3(-2) = 0$

$x - 4 = 0$

$x = +4$

**(xiv)** The algebric sum of oxidation state of all the atoms in a polyatomic ion is equal to the charge present on the ion.

Ex. $SO_4^{-2}$

If O.S of S is x then

$x + 4(-2) = -2$

$x - 6 = 0$

$x = +6$

Ex. $HCO_3^-$

If O.S of C is x then

$+1 + x + 3(-2) = -1$

$x - 4 = 0$

$x = +4$

**(B) In case of co-ordinate bond (EN of B > A) :**

$$\begin{array}{lcccccccc} & A \rightarrow & AB \rightarrow & B & A \rightarrow & B & B \rightarrow & A & \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{O.S.:} & +2 & -2 & +2 & -2 & +2 & -2 & O & O \end{array}$$

**(C) In case of Ionic bond :**

Charge on cation = O.S of cation

Charge on anion = O.S of anion

$$\begin{array}{llccc} \text{Ex.} & NaCl \rightarrow & Na^+ & + & Cl^- \\ & & \downarrow & & \downarrow \\ & & +1 & & -1 \\ & MgCl_2 \rightarrow & Mg^{+2} & + & 2Cl^- \\ & & \downarrow & & \downarrow \\ & & +2 & & -1 \end{array}$$

**APPLICATIONS OF OXIDATION NUMBER :**

## (A) To compare the strength of acid and base :

Strength of acid $\alpha$ Oxidation Number

Strength of base $\alpha$ $\dfrac{1}{\text{Oxidation Number}}$

**Example :** Order of acidic strength in HClO, $HClO_2$, $HClO_3$, $HClO_4$ will be.

**Solution :**

| | Oxidation Number of chlorine |
|---|---|
| HClO (Hypo chlorous acid) | +1 |
| $HClO_2$ (Chlorous acid) | +3 |
| $HClO_3$ (Chloric acid) | +5 |
| $HClO_4$ (Perchloric acid) | +7 |

$\because$ Strength of acid $\alpha$ Oxidation Number

So the order will be -

$HClO_4 > HClO_3 > HClO_2 > HClO$

**(B) To determine the oxidising and reducing nature of the substances :**

**Oxidising agents** are the substances which accept electrons in a chemical reaction i.e., electron acceptors are oxidising agent.

**Reducing agents** are the substances which donate electrons in a chemical reaction i.e., electron donors are reducing agent.

| **Highest O.S.** | +4 | +5 | +5 | +6 | +7 | +6 | +7 | +8 | +8 | +2 | +1 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Elements** | C | N | P | S | Cl | Cr | Mn | Os | Ru | O | H |
| **Lowest O.S.** | -4 | -3 | -3 | -2 | -1 | 0 | 0 | 0 | 0 | -2 | -1 |

(a) If effective element in a compound is present in maximum oxidation state then the compound acts as oxidising agent.

Ex. $\underset{+7}{\underset{\downarrow}{KMnO_4}}$ $\underset{+6}{\underset{\downarrow}{K_2Cr_2O_7}}$ $\underset{+6}{\underset{\downarrow}{H_2SO_4}}$ $\underset{+6}{\underset{\downarrow}{SO_3}}$ $\underset{+5}{\underset{\downarrow}{H_3PO_4}}$ $\underset{+5}{\underset{\downarrow}{HNO_3}}$ $\underset{+7}{\underset{\downarrow}{HClO_4}}$

(b) If effective element in a compound is present in minimum oxidation state then the compound acts as reducing agent.

$\underset{-3}{\underset{\downarrow}{PH_3}}$ $\underset{-3}{\underset{\downarrow}{NH_3}}$ $\underset{-4}{\underset{\downarrow}{CH_4}}$

(c) If effective element in a compound is present in intermediate oxidation state then the compound can act as oxidising agent as well as reducing agent.

$\underset{+3}{\underset{\downarrow}{HNO_2}}$ $\underset{+3}{\underset{\downarrow}{H_3PO_3}}$ $\underset{+4}{\underset{\downarrow}{SO_2}}$ $\underset{-1}{\underset{\downarrow}{H_2O_2}}$

**(C) To calculate the equivalent weight of compounds :**

The equivalent weight of an oxidising agent or reducing agent is that weight which accepts or loses one mole electrons in a chemical reaction.

(a) Equivalent weight of oxidant = $\dfrac{\text{Molecular weight}}{\text{No. of electrons gained by one mole}}$

**Example :** In acidic medium

$$6e^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Here atoms which undergoes reduction is Cr. Its O. S. is decreasing from +6 to +3

$$\text{Equivalent weight of } K_2Cr_2O_7 = \frac{\text{Molecular weight of } K_2Cr_2O_7}{3 \times 2} = \frac{M}{6}$$

**Note :- [**6 in denominator indicates that 6 electrons were gained by $Cr_2O_7^{2-}$ as it is clear from the given balanced equation**]**

(b) Equivalent weight of a reducant = $\dfrac{\text{Molecular weight}}{\text{No. of electrons lost by one mole}}$

In acidic medium, $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

Here, atoms which undergoes oxidation is C. Its oxidation state is increasing from +3 to +4.

Here, Total electrons lost in $C_2O_4^{-2}$ = 2 So, equivalent weight of $C_2O_4^{-2} = \dfrac{M}{2}$

(c) In different conditions a compound may have different equivalent weight because, it depends upon the number of electrons gained or lost by that compound in that reaction.

**Example :**

(i) $\underset{(+7)}{MnO_4^-} \longrightarrow \underset{(+2)}{Mn^{+2}}$ (acidic medium)

Here 5 electrons are taken by $MnO_4^-$ so its equivalent weight = $\dfrac{M}{5} = \dfrac{158}{5} = 31.6$

(ii) $MnO_4^- \longrightarrow MnO_2$ (neutral medium) or (Weak alkaline medium)
(+7) (+4)

Here, only 3 electrons are gained by $MnO_4^-$ so its equivalent weight = $\frac{M}{3} = \frac{158}{3} = 52.7$

**Note :** When only alkaline medium is given consider it as weak alkaline medium.

(iii) $MnO_4^- \longrightarrow MnO_4^{-2}$ (strong alkaline medium)
(+7) (+6)

Here, only one electron is gained by $MnO_4^-$ equivalent weight = $\frac{M}{1}$ = 158

**Note :-** $KMnO_4$ acts as an oxidant in every medium although with different strength which follows the order –

acidic medium > neutral medium > alkaline medium

while, $K_2Cr_2O_7$ acts as an oxidant only in acidic medium as follows

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$
$(2 \times 6) \longrightarrow (2 \times 3)$

Here, 6 electrons are gained by $K_2Cr_2O_7$ equivalent weight = $\frac{M}{6} = \frac{294}{6} = 49$

**(D) To determine the possible molecular formula of compound :**
Since the sum of oxidation number of all the atoms present in a compound is zero, so the validity of the formula can be confirmed.

## POINTS TO REVISE

**SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQUIVALENT WEIGHT :**

| Species | Changed to | Reaction | Electrons exchanged or change in O.N. | Eq. wt. |
|---|---|---|---|---|
| $MnO_4^-$(O.A.) | $Mn^{+2}$ in acidic medium | $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | 5 | $E = \frac{M}{5}$ |
| $MnO_4^-$(O.A.) | $MnO_2$ in neutral medium or in weak alkaline medium | $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$ | 3 | $E = \frac{M}{3}$ |
| $MnO_4^-$(O.A.) | $MnO_4^{2-}$ in strong alkaline medium | $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$ | 1 | $E = \frac{M}{1}$ |
| $Cr_2O_7^{2-}$(O.A.) | $Cr^{3+}$ in acidic medium | $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ | 6 | $E = \frac{M}{6}$ |
| $MnO_2$(O.A.) | $Mn^{2+}$ in acidic medium | $MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$ | 2 | $E = \frac{M}{2}$ |
| $Cl_2$(O.A.) in bleaching powder | $Cl^-$ | $Cl_2 + 2e^- \longrightarrow 2Cl^-$ | 2 | $E = \frac{M}{2}$ |
| $CuSO_4$(O.A.) in iodometric titration | $Cu^+$ | $Cu^{2+} + e^- \longrightarrow Cu^+$ | 1 | $E = \frac{M}{1}$ |
| $S_2O_3^{2-}$ (R.A.) | $S_4O_6^{2-}$ | $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$ | 2 (for two moles) | $E = \frac{2M}{2} = M$ |
| $H_2O_2$(O.A.) | $H_2O$ | $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ | 2 | $E = \frac{M}{2}$ |
| $H_2O_2$(R.A.) | $O_2$ | $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ (O.N. of oxygen in $H_2O_2$ is –1 per atom) | 2 | $E = \frac{M}{2}$ |
| $Fe^{2+}$(R.A.) (R.A) | $Fe^{3+}$ (in acidic medium) | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ | 1 (for two moles) | $E = \frac{M}{1}$ |
| $I^-$ | $I_2$ | $2I^- \longrightarrow I_2 + 2e^-$ | 2 | $E = \frac{M}{1}$ |
| $I^-$ (R.A) | $IO_3^-$ (in basic medium) | $I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$ | 6 | $E = \frac{M}{6}$ |

**OXIDATION AND REDUCTION :**

There are two concepts of oxidation and reduction.

**(A) Classical/old concept :**

| | **OXIDATION** | **REDUCTION** |
|---|---|---|
| (1) | Addition of $O_2$ | Addition of $H_2$ |
| | $2Mg + O_2 \rightarrow 2MgO$ | $N_2 + 3H_2 \rightarrow 2NH_3$ |
| | $C + O_2 \rightarrow CO_2$ | $H_2 + Cl_2 \rightarrow 2HCl$ |
| (2) | Removal of $H_2$ | Removal of $O_2$ |
| | $H_2S + Cl_2 \rightarrow 2HCl + S$ (oxidation of $H_2S$) | $CuO + C \rightarrow Cu + CO$ (reduction of CuO) |
| | $4HI + O_2 \rightarrow 2I_2 + 2H_2O$ (oxidation of HI) | $H_2O + C \rightarrow CO + H_2$ (reduction of $H_2O$) |
| (3) | Addition of electronegative element | Addition of electropositive element |
| | $Fe + S \rightarrow FeS$ (oxidation of Fe) | $CuCl_2 + Cu \rightarrow Cu_2Cl_2$ (reduction of $CuCl_2$) |
| | $SnCl_2 + Cl_2 \rightarrow SnCl_4$ (oxidation of $SnCl_2$) | $HgCl_2 + Hg \rightarrow Hg_2Cl_2$ (reduction of $HgCl_2$) |
| (4) | Removal of electropositive element | Removal of electronegative element |
| | $2NaI + H_2O_2 \rightarrow 2NaOH + I_2$ (oxidation of NaI) | $2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$ (reduction of $FeCl_3$) |

**(B) Electronic/Modern Concept :**

| | **OXIDATION** | **REDUCTION** |
|---|---|---|
| (1) | De-electronation | Electronation |
| (2) | Oxidation process are those process in which one or more $e^-$s are lost by an atom, ion or molecule. | Reduction process are those process in which one or more $e^-$s are gained by an atom, ion or molecule. |
| (3) | Example - | |
| | (a) $Zn \rightarrow Zn^{+2} + 2e^-$ | $Cu^{+2} + 2e^- \rightarrow Cu$ |
| | $M \rightarrow M^{n+} + ne^-$ | $M^{n+} + ne^- \rightarrow M$ |
| | (b) $Sn^{+2} \rightarrow Sn^{+4} + (4-2)\,e^-$ | $Fe^{+3} + (3-2)\,e^- \rightarrow Fe^{+2}$ |
| | $M^{+n_1} \rightarrow M^{+n_2} + (n_2-n_1)e^-$ | $M^{+x_1} + (x_1-x_2)e^- \rightarrow M^{+x_2}$ |
| | (c) $Cl^- \rightarrow Cl + e^-$ | $O + 2e^- \rightarrow O^{2-}$ |
| | $A^{-n} \rightarrow A + ne^-$ | $A + xe^- \rightarrow A^{-x}$ |
| | (d) $MnO_4^{-2} \rightarrow MnO_4^- + (2-1)e^-$ | $[Fe(CN)_4]^{3-} + (4-3)e^- \rightarrow [Fe(CN)_4]^{-4}$ |
| | $A^{-n_1} \rightarrow A^{-n_2} + (n_1-n_2)e^-$ | $A^{-n_1} + (n_2-n_1)e^- \rightarrow A^{-n_2}$ |

**TYPES OF REDOX REACTIONS :**

**(A) Intermolecular redox reaction :-** When oxidation and reduction takes place separately in different compounds, then the reaction is called intermolecular redox reaction.

$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$

$Sn^{+2} \longrightarrow Sn^{+4}$ (Oxidation)

$Fe^{+3} \longrightarrow Fe^{+2}$ (Reduction)

**(B) Intramolecular redox reaction :-** During the chemical reaction, if oxidation and reduction takes place in single compound then the reaction is called intramolecular redox reaction.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

$$Cl^{+5}O^{-2} \qquad Cl^{-1} \qquad O^{\circ}$$

Reduction

Oxidation

**(C) Disproportionation reaction :-** When reduction and oxidation takes place in the same element of the same compound then the reaction is called disproportionation reaction.

$$H_2O_2 \longrightarrow H_2O + 1/2\ O_2$$

$$O^{-1} \qquad\qquad O^{-2} \qquad O^{\circ}$$

Reduction

Oxidation

**(D) Comproportionation reaction:** Reverse of disproportionation reaction known as comproportionation reaction. **Ex.** $HClO + Cl^- \rightarrow Cl_2 + OH^-$

**BALANCING OF REDOX REACTION :**

(A) Oxidation number change method.

(B) Ion electron method.

**(A) Oxidation number change method :**

This method was given by Johnson. In a balanced redox reaction, total increase in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basis for balancing redox reactions.

The general procedure involves the following steps :

(i) Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.

(ii) Select the atom in reducing agent whose oxidation number increases and indicate the loss of electrons.

(iii) Now cross multiply i.e.multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.

(iv) Balance the number of atoms on both sides whose oxidation numbers change in the reaction.

(v) In order to balance oxygen atoms, add $H_2O$ molecules to the side deficient in oxygen.

(vi) Then balance the number of H atoms by adding $H^+$ ions to the side deficient in hydrogen.

## Illustrations

**Illustration** Balance the following reaction by the oxidation number method –

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

**Solution** Write the oxidation number of all the atoms.

$$\overset{0}{Cu} + \overset{+1+5-2}{HNO_3} \longrightarrow \overset{+2+5-2}{Cu(NO_3)_2} + \overset{+4\ -2}{NO_2} + \overset{+1-2}{H_2O}$$

There is change in oxidation number of Cu and N.

$$\overset{0}{Cu} \longrightarrow \overset{+2+5-2}{Cu(NO_3)_2} \quad \text{.........................(1) (Oxidation no. is increased by 2)}$$

$$\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2} \quad \text{.........................(2) (Oxidation no. is decreased by 1)}$$

To make increase and decrease equal, eq. (2) is multiplied by 2.

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

Balancing nitrates ions, hydrogen and oxygen, the following equation is obtained.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

This is the balanced equation.

**Illustration** Balance the following reaction by the oxidation number method –

$$MnO_4^- + Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$$

**Solution** Write the oxidation number of all the atoms.

$+7\ -2$

$MnO_4^- + \quad Fe^{+2} \xrightarrow{\qquad\qquad} Mn^{+2} + Fe^{+3}$

change in oxidation number has occured in Mn and Fe.

$+7$

$MnO_4^- \longrightarrow Mn^{+2}$ ..........................(1) (Decrement in oxidation no. by 5)

$Fe^{+2} \longrightarrow Fe^{+3}$ ..........................(2) (Increment in oxidation no. by 1)

To make increase and decrease equal, eq. (2) is multiplied by 5.

$MnO_4^- + 5Fe^{+2} \longrightarrow Mn^{+2} + 5Fe^{+3}$

To balance oxygen, $4H_2O$ are added to R.H.S. and to balance hydrogen, $8H^+$ are added to L.H.S.

$MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$

This is the balanced equation.

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**(B) Ion-Electron method :-**

This method was given by Jette and La Mev in 1972.

The following steps are followed while balancing redox reaction (equations) by this method.

(i) Write the equation in ionic form.

(ii) Split the redox equation into two half reactions, one representing oxidation and the other representing reduction.

(iii) Balance these half reactions separately and then add by multiplying with suitable coefficients so that the electrons are cancelled. Balancing is done using following substeps.

(a) Balance all other atoms except H and O.

(b) Then balance oxygen atoms by adding $H_2O$ molecules to the side deficient in oxygen. The number of $H_2O$ molecules added is equal to the deficiency of oxygen atoms.

(c) Balance hydrogen atoms by adding $H^+$ ions equal to the deficiency in the side which is deficient in hydrogen atoms.

(d) Balance the charge by adding electrons to the side which is rich in +ve charge. i.e. deficient in electrons. Number of electrons added is equal to the deficiency.

(e) Multiply the half equations with suitable coefficients to equalize the number of electrons.

(iv) Add these half equations to get an equation which is balanced with respect to charge and atoms.

(v) If the medium of reaction is basic, $OH^-$ ions are added to both sides of balanced equation, which is equal to number of $H^+$ ions in Balanced Equation.

## Illustrations

**Illustration** Balance the following reaction by ion-electron method in acidic medium :

$$Cr_2O_7^{2-} + C_2O_4^{2-} \longrightarrow Cr^{3+} + CO_2$$

**Solution** $Cr_2O_7^{2-} + C_2O_4^{2-} \longrightarrow Cr^{3+} + CO_2$

(a) Write both the half reaction.

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ (Reduction half reaction)

$C_2O_4^{2-} \longrightarrow CO_2$ (Oxidation half reaction)

(b) Atoms other than H and O are balanced.

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

$C_2O_4^{2-} \longrightarrow 2CO_2$

(c) Balance O-atoms by the addition of $H_2O$ to another side

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

$C_2O_4^{2-} \longrightarrow 2CO_2$

(d) Balance H-atoms by the addition of $H^+$ to another side

$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

$C_2O_4^{2-} \longrightarrow 2CO_2$

(e) Now, balance the charge by the addition of electron ($e^-$).

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ .......(1)

$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ .......(2)

(f) Multiply equations by a constant to get the same number of electrons on both side. In the above case second equation is multiplied by 3 and then added to first equation.

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^-$

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$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

**Illustration** Balance the following reaction by ion-electron method :

$$Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} I^- + CrO_4^{2-}$$

**Solution** $Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} I^- + CrO_4^{2-}$

(a) Separate the two half reactions.

$Cr(OH)_3 \longrightarrow CrO_4^{2-}$ (Oxidation half reaction)

$IO_3^- \longrightarrow I^-$ (Reduction half reaction)

(b) Balance O-atoms by adding $H_2O$.

$H_2O + Cr(OH)_3 \longrightarrow CrO_4^{2-}$

$IO_3^- \longrightarrow I^- + 3H_2O$

(c) Balance H-atoms by adding $H^+$ to side having deficiency and add equal no. of $OH^-$ ions to the side ($\because$ medium is known)

$$H_2O + Cr(OH)_3 \longrightarrow CrO_4^{-2} + 5H^+$$

$$5OH^- + H_2O + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 5H^+ + 5OH^-$$

or $$5OH^- + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 4H_2O$$

$$IO_3^- + 6H^+ \longrightarrow I^- + 3H_2O$$

$$IO_3^- + 6H^+ + 6OH^- \longrightarrow I^- + 3H_2O + 6OH^-$$

or $$IO_3^- + 3H_2O \longrightarrow I^- + 6OH^-$$

(d) Balance the charges by adding electrons

$$5OH^- + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 4H_2O + 3e^-$$

$$IO_3^- + 3H_2O + 6e^- \longrightarrow I^- + 6OH^-$$

(e) Multiply first equation by 2 and add to second to give

$$10OH^- + 2Cr(OH)_3 \longrightarrow 2CrO_4^{2-} + 8H_2O + 6e^-$$

$$IO_3^- + 3H_2O + 6e^- \longrightarrow I^- + 6OH^-$$

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**LAW OF EQUIVALENCE**

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equal number of equivalents or milli equivalents of reactants react to give equal number of equivalents or milli equivalents of products separately.

**According :**

(i) $aA + bB \rightarrow mM + nN$

m. eq of A = number of m. eq of B = number of m. eq of M = number of m. eq of N

(ii) In a compound $M_xN_y$

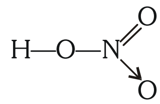
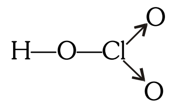
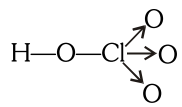
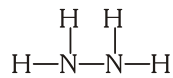
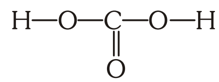
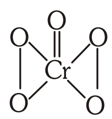
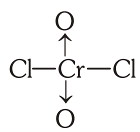
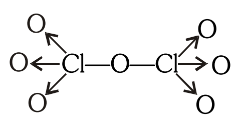
Number of m. eq of $M_xN_y$ = m.eq of M = number of m.eq of N

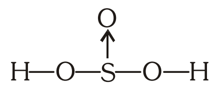
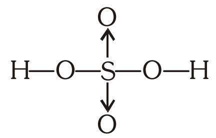
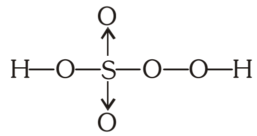
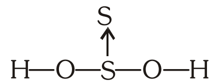
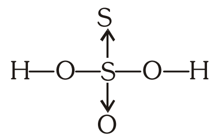
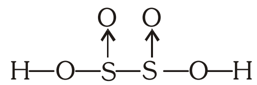
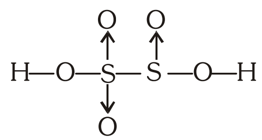
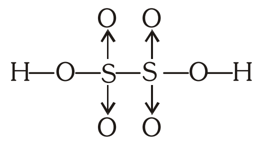
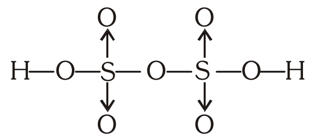
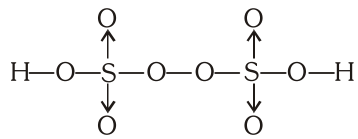
## POINTS TO REVISE

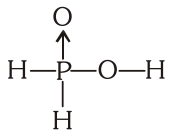
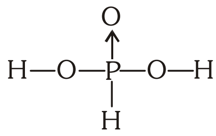
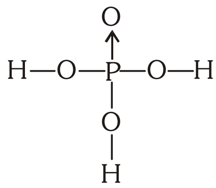
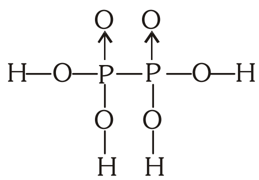
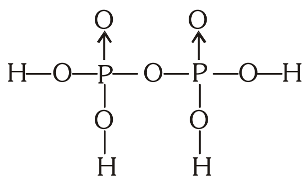
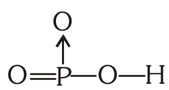
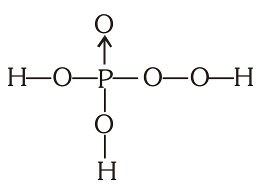
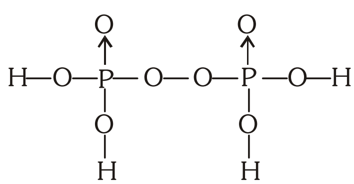
- **FOR REDOX REACTIONS :**

$N_1V_1 = N_2V_2$ is always true.

But $(M_1 \times V_1) \times n_1 = (M_2 \times V_2) \times n_2$ (always true where n term represents valency factor).

| LINE STRUCTURE OF SOME COMPOUNDS | | | | Oxidation state |
|---|---|---|---|---|
| 1. | Hydrogen peroxide | $H_2O_2$ | H — O — O — H | O = ……… |
| 2. | Nitrous acid | $HNO_2$ | H—O—N=O | N = ……… |
| 3. | Nitric acid | $HNO_3$ |  | N = ……… |
| 4. | Hypo chlorous acid | HClO | H—O—Cl | Cl = …….. |
| 5. | Chlorous acid | $HClO_2$ | H —O—Cl →O | Cl = …….. |
| 6. | Chloric acid | $HClO_3$ |  | Cl = …….. |
| 7. | Perchloric acid | $HClO_4$ |  | Cl = …….. |
| 8. | Hydrazine | $N_2H_4$ |  | N = …….. |
| 9. | Carbonic acid | $H_2CO_3$ |  | C= …….. |
| 10. | Chromium pentoxide | $CrO_5$ |  | Cr = …….. |
| 11. | Nitrosyl chloride/ Tilden's reagent | NOCl | Cl—N=O | N = …….. |
| 12. | Chromyl chloride | $CrO_2Cl_2$ |  | Cr = …….. |
| 13. | Perchloric anhydride | $Cl_2O_7$ |  | Cl = …….. |
| 14. | Calcium oxy-chloride/ Bleaching powder | $CaOCl_2$ | Ca(O*Cl)**Cl | *Cl = ……..<br>**Cl = …….. |

| OXY ACIDS OF SULPHUR | | | | O.S. of central Sulphur atom |
|---|---|---|---|---|
| 1. | Sulphoxilic acid | $H_2SO_2$ | H—O—S—O—H | |
| 2. | Sulphurous acid | $H_2SO_3$ |  | |
| 3. | Sulphuric acid | $H_2SO_4$ |  | |
| 4. | Peroxymonosulphuric acid (Caro's acid) | $H_2SO_5$ |  | |
| 5. | Thiosulphurous acid | $H_2S_2O_2$ |  | |
| 6. | Thiosulphuric acid | $H_2S_2O_3$ |  | |
| 7. | Dithionous acid | $H_2S_2O_4$ |  | |
| 8. | Pyrosulphurous acid | $H_2S_2O_5$ |  | |
| 9. | Dithionic acid | $H_2S_2O_6$ |  | |
| 10. | Pyrosulphuric acid/ Fuming sulphuric acid/ Oleum | $H_2S_2O_7$ |  | |
| 11. | Peroxydisulphuric acid (Marshal's acid) | $H_2S_2O_8$ |  | |

| OXY ACIDS OF PHOSPHOROUS | | | | **O.S. of central P atom** |
|---|---|---|---|---|
| 1. | Hypophophorous acid | $H_3PO_2$ |  | |
| 2. | Orthophosphorous acid/ Phophorous acid | $H_3PO_3$ |  | |
| 3. | Orthophosphoric acid/ Phophoric acid | $H_3PO_4$ |  | |
| 4. | Hypophosphoric acid | $H_4P_2O_6$ |  | |
| 5. | Pyrophosphoric acid | $H_4P_2O_7$ |  | |
| 6. | Metaphosphoric acid | $HPO_3$ |  | |
| 7. | Peroxymonophosphoric acid | $H_3PO_5$ |  | |
| 8. | Peroxydiphosphoric acid | $H_4P_2O_8$ |  | |